

Inexpensive Vibrational Anharmonicities from Estimated Derivatives: Diatomic Molecules

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ABSTRACT: Four alternatives are compared for estimating vibrational anharmonicity constants without explicitly calculating the expensive fourth derivatives of the potential curves. In the first, semiempirical approach, fourth derivatives for 53 diatomic molecules are estimated from *ab initio* second and third derivatives by using the Morse model potential. Vibrational anharmonicities $\omega_e x_e$ are then computed from the third and fourth derivatives. The second approach invokes a purely empirical linear correlation between $\omega_e x_e$ and the harmonic frequencies ω_e . The third and fourth empirical approaches suppose that the effective harmonic and anharmonic force constants are proportional (with an additive constant in the fourth approach). Experimental values for $\omega_e x_e$ are compared with empirical predictions and with semiempirical estimates based upon Hartree–Fock (HF), Møller–Plesset (MP2), and local, nonlocal, and hybrid density-functional theories (DFT), using the small 6-31G* basis set. *Ab initio* values of ω_e and bond lengths r_e are also compared against experiment. The (U)MP2 results are the worst and include several anomalies. The other semiempirical methods yield results of comparable accuracy for $\omega_e x_e$ of hydrides, although the DFT methods are markedly better for ω_e and r_e and for $\omega_e x_e$ of nonhydrides. The empirical estimates are nearly as good as the semiempirical ones. We conclude that: (1) both empirical and semiempirical approximations are useful for predicting stretching anharmonicity constants $\omega_e x_e$ to precisions of $\sigma \approx 5 \text{ cm}^{-1}$ for hydrides and $\sigma \approx 1.5 \text{ cm}^{-1}$ for nonhydrides; and (2) MP2 theory is relatively unreliable for such calculations. In addition, we find the following tests to be useful when evaluating the reliability of vibrational constants calculated at the UMP2 level: (a) the calculated values of

ω_e and $\omega_e x_e$ should not deviate substantially from the empirical relations; (b) harmonic frequencies and intensities calculated at the MP2 level should be smaller than those calculated at the corresponding HF level; (c) a large distance-dependence of the spin contamination, $d\langle S^2 \rangle/dR \gtrsim 0.05 \text{ \AA}^{-1}$, suggests that calculated constants are too large. © 1998 John Wiley & Sons, Inc. J Comput Chem 19: 1315–1324, 1998

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Introduction

High-level *ab initio* calculations typically reproduce experimentally extrapolated harmonic vibrational frequencies (ω_e) to an accuracy of 10 cm^{-1} or better ($1 \text{ cm}^{-1} = 0.012 \text{ kJ/mol}$).¹ However, the anharmonic effects on the fundamental frequency (ω_0) can exceed 100 cm^{-1} , resulting in poor predictions ($\omega_0 = \omega_e - 2\omega_e x_e$ for a diatomic molecule). Because the fundamental frequencies are the observed quantities in ordinary vibrational spectroscopy, vibrational anharmonicities are important for comparisons between predictions and observations. Thus, the target accuracy for anharmonicity constants ($\omega_e x_e$) is 5 cm^{-1} or better. Anharmonic effects are even stronger for the higher harmonics, which are typically in the near infrared (NIR).

Anharmonic vibrational effects are also relevant to thermochemistry. As *ab initio* methods become increasingly accurate at treating the electronic part of the problem, errors in the vibrational treatment grow in significance.² Thermal functions such as entropy and heat capacity are derived from the molecular partition function, which is directly affected by vibrational anharmonicity. More importantly, vibrational zero-point energies (ZPEs) are more reliably predicted if anharmonicity constants are available. Although the effect on any single vibration is small, in polyatomic molecules the total ZPE is the sum over all vibrations. Thus, it is important to avoid systematic errors in predicted anharmonicity constants, so that errors do not accumulate.

Vibrational anharmonicities are typically calculated using vibrational perturbation theory,^{3,4} although variational calculations are practical for small molecules.^{5,6} Fortunately, although inexpensive, Hartree–Fock (HF) theory generally overesti-

mates second derivatives (i.e., harmonic vibrational frequencies),^{7,8} higher derivatives often agree well with those calculated using expensive, correlated electronic wave functions.^{9–11} This indicates that a low-level theory can be used to compute anharmonicities while using a more expensive calculation to determine the harmonic frequencies. This type of hybrid method has been demonstrated successfully.^{12,10}

Unfortunately, even HF anharmonicities are very expensive. This is because both the third and fourth derivatives of the molecular potential energy surface are needed to predict anharmonicities reliably; the contributions of the third and fourth derivatives are of opposite sign but of comparable magnitude. Moreover, although analytic derivative methodology and computer programs do exist,^{10,13} none of the readily available software packages has the capability to compute these higher derivatives.

We are interested in developing methods to permit vibrational anharmonicities to be computed routinely and at reasonable cost. Because the most expensive step is the calculation of the fourth derivatives, we would like to circumvent this. Our initial, semiempirical approach is to use a model potential to estimate the fourth derivatives based on the values of the lower derivatives. The simplest case is diatomic molecules; the Morse oscillator is a good model potential and contains only three parameters, as required. The Morse potential has occasionally been applied in this way before, but not used or studied systematically as in the present work. In this article, we examine the validity of the approximation and also investigate a number of inexpensive *ab initio* methods for their performance in the prediction of stretching anharmonicities.

We also consider three methods that avoid calculating both the third and fourth derivatives, saving even more expense. The first of these involves a purely empirical, approximate, linear cor-

relation between $\omega_e x_e$ and ω_e . The second is based on the approximation that the effective harmonic and anharmonic force constants are proportional. The third builds upon the second by including an additive constant. In practice, these methods would best be combined with high-quality calculations of the harmonic vibrational frequencies.

High-frequency vibrations dominate the vibrational zero-point energy in molecules. In contrast, low-frequency vibrations dominate the vibrational partition function and the corresponding thermodynamic functions. When extended to polyatomic molecules and combined with high-level harmonic frequencies, the methods in this article for estimating $\omega_e x_e$ are therefore expected to be useful for ZPE calculations involving hydrogenic stretches and for thermodynamic functions of molecules containing heavy-atom stretches. For diatomic molecules, the vibrational levels and ZPE are given in eq. (1), where ν is the quantum number:

$$\epsilon(\nu) = \omega_e \left(\nu + \frac{1}{2} \right) - \omega_e x_e \left(\nu + \frac{1}{2} \right)^2$$

$$\left(\text{so ZPE} = \frac{1}{2} \omega_e - \frac{1}{4} \omega_e x_e \right) \quad (1)$$

Computational Methods

All calculations were on molecules in their electronic ground states, as designated in the experimental literature. All energy derivatives were computed at the corresponding energy minima, which were obtained using the default convergence criteria.^{14,15} Analytic second derivatives and numerical third derivatives were computed as coded in the GAUSSIAN-92/DFT program package.^{14,16} When DFT convergence problems were encountered, the Gaussian-94 program was used instead.^{16,17} For RMP2 and UMP2 calculations, third derivatives were determined by central differences of analytic second derivatives, using a step size of 0.001 Å. In the cases where anomalous UMP2 results were obtained, spin-restricted open-shell MP2 (ROMP2) calculations were done using the ACES II program suite.^{15,16,18} Numerical ROMP2 second derivatives were determined from analytic gradients as coded in the ACES II package, and third derivatives were determined from these Hessians using central differences and a step

size of 0.02 bohr (1 bohr = 5.291772×10^{-11} m). MP2 calculations done using GAUSSIAN-92/DFT were frozen-core; those done using ACES II included all electrons in the correlation treatment.

The DFT calculations involve a grid upon which the density functional is integrated numerically. The default grid in GAUSSIAN-92/DFT ("SG1Grid") often yields values of $\omega_e x_e$ that differ markedly from those obtained using the default grid in GAUSSIAN-94 ("FineGrid"). For the SH molecule; for example, we obtained $\omega_e x_e = 75.9 \text{ cm}^{-1}$ using "SG1Grid," 60.3 cm^{-1} using "FineGrid," 54.4 cm^{-1} using a "99-302" grid, and 54.8 cm^{-1} using a "benchmark" grid. Identical results were obtained using unpruned versions of the first two grids. Thus, the "FineGrid" grid (the GAUSSIAN-94 default) does not appear to be converged. However, it is much less expensive than the "99-302" grid. Because the purpose of this study is to seek inexpensive methods, we accept the approximate "FineGrid" option.

To permit extension of our results to large molecules, all computations used the small 6-31G* basis sets. Spin-unrestricted methods were used for open-shell molecules. The *ab initio* methods used were Hartree-Fock (HF), second-order perturbation theory (MP2), and the density-functional methods denoted SVWN, BLYP, and Becke3LYP (also commonly denoted B3LYP) in the Gaussian-92/DFT package.^{14,16} Only the valence electrons were correlated in the MP2 calculations. SVWN is local, employing Slater's exchange functional ($\alpha = 2/3$)¹⁹ and the Vosko-Wilk-Nusair correlation functional.²⁰ BLYP employs the nonlocal (gradient-corrected) Becke-88 exchange²¹ and Lee-Yang-Parr correlation²² functionals. B3LYP is a hybrid HF-DFT functional²³ that also uses the Becke-88 and Lee-Yang-Parr functionals, and is closely related to the three-parameter functional that Becke optimized for the thermochemistry of small molecules.²⁴ Note that the DFT methods include electron correlation in a self-consistent manner.

The Morse potential, eq. (2), can be used to estimate the fourth derivative according to eq. (3), and the anharmonicity constant $\omega_e x_e$ can be computed by perturbation theory.²⁵ This result is the same as that obtained from exact eigenfunctions of the Morse oscillator²⁵ and is given by eq. (4), where μ is the reduced mass in amu (1 amu = 1.660540×10^{-27} kg), the energy derivatives are in atomic units (1 hartree = 4.359748×10^{-18} J), and $\omega_e x_e$ is in cm^{-1} . Since the anharmonicity constant

depends upon a ratio of derivatives [eq. (4)], one would expect some cancellation of systematic errors, leading to more reliable predictions of $\omega_e x_e$ than of the bare derivatives:

$$U(r) = D_e[1 - \exp(-\beta(r - r_e))]^2 \quad (2)$$

$$U^{iv} = \frac{7}{9} \frac{(U''')^2}{U''} \text{ at } r = r_e \quad (3)$$

$$\omega_e x_e = \frac{6.689}{\mu} \left(\frac{U'''}{U''} \right)^2 \quad (4)$$

As one alternative, empirical means for estimating $\omega_e x_e$, we note the approximate linear correlation between $\omega_e x_e$ and ω_e given in eq. 5. A more physically-motivated alternative is provided by eq. 6, in which μ is the reduced mass of the molecule. Eq. 6 is motivated by the mass-scaling of the spectroscopic constants, as in eq. 4, in combination with the approximation that the effective harmonic and anharmonic force constants are proportional. The inverse mass dependence reflects the fact that light atoms sample distant parts of the potential, where anharmonic effects are accentuated. The standard errors of the fits, which were obtained using experimental values of the spectroscopic constants, are 6.9 cm^{-1} (for 14 hydrides) and 1.7 cm^{-1} (for 38 nonhydrides) for eq. 5 and 6.2 cm^{-1} (hydrides) and 1.6 cm^{-1} (nonhydrides) for eq. 6. Thus, eq. 6 fits the experimental data as well as eq. 5 despite using only a single adjustable parameter.

A combination of eqs. 5 and 6 leads to empirical eq. 7, which fits the experimental data best by a small margin (standard error = 5.8 cm^{-1} for hydrides and 1.5 cm^{-1} for nonhydrides). Because eqs. (5)–(7) avoid

$$\omega_e x_e \approx a \cdot \omega_e + b \quad (5)$$

$$\omega_e x_e \approx A \cdot \omega_e \cdot \mu^{-1/2} \quad (6)$$

$$\omega_e x_e \approx A' \cdot \omega_e \cdot \mu^{-1/2} + B \quad (7)$$

even the third derivatives, they merit comparison with the more expensive Morse-model approach described above.

Results

The experimental and computed equilibrium bond lengths, r_e , are collected in Table I. The

experimental and computed harmonic vibrational frequencies, ω_e , are collected in Table II. The experimental and computed (eq. 4) harmonic vibrational anharmonicities, $\omega_e x_e$, are collected in Table III. Errors relative to experimental values are expressed absolutely (in cm^{-1}) for $\omega_e x_e$ and fractionally (as a percentage) for ω_e and r_e . Table IV summarizes the performance of the various methods and also includes the values of the parameters in eqs. 5–7. In Table IV, statistics for $\omega_e x_e$ are computed separately for hydrides and nonhydrides because of the large difference in magnitude for the different types of molecule. Mean errors indicate empirically correctable, systematic, signed error and standard deviations measure the scatter around the mean. For r_e and ω_e , error statistics are computed using the full set of molecules and also by excluding the results for the weakly bound Be_2 molecule, for which the conventional, wave-function-based methods (HF and MP2) perform exceptionally poorly. For $\omega_e x_e$, error statistics are computed using the full data set and also by excluding the results for the H_2 and Be_2 molecules, for which all five methods perform poorly. We choose not to tabulate 6-31G* results for ω_0 and ZPE because it is unprofitable to apply anharmonicity corrections to crude (e.g., 6-31G*) values of ω_e ; anharmonic effects limit the accuracy only of high-level frequency calculations. Thus, Table IV also includes the performance of eqs. (5)–(7) when applied to experimental values of ω_e . In practice, ω_e would be obtained using high-level *ab initio* calculations.

Discussion

Accurate predictions are indicated in Table IV by small mean unsigned errors (MUE), defined as the mean of the absolute values of the deviations from experiment. Systematic, signed errors are indicated by the mean (signed) errors. Precise (i.e., consistent) predictions are indicated by small standard deviations. Of the five semiempirical procedures tested, the best bond lengths (r_e) are obtained with the SVWN and B3LYP methods, which give mean unsigned errors of 1.5% and 1.2%, respectively. When Be_2 is excluded all the methods give results good to 2% (Table IV). The B3LYP hybrid method provides the best harmonic frequencies (ω_e), with the other two DFT methods

TABLE I.
Errors in Bond Length r_e . Experimental Values from Ref. 35 Unless Otherwise Noted.

	Expt. (Å)	Deviation from expt. (%)					Expt. (Å)		Deviation from expt. (%)				
		UHF	UMP2	SVWN	BLYP	B3LYP			UHF	UMP2	SVWN	BLYP	B3LYP
FH	0.917	-0.6	1.9	2.4	3.1	1.9	SiO	1.510	-1.5	2.2	1.1	2.3	0.9
OH	0.970	-1.2	1.0	2.2	2.6	1.4	PO	1.476	-1.4	-0.3	1.8	3.1	1.5
NH	1.036	-1.2	0.3	2.3	2.3	1.1	SO	1.481	-1.0	3.0	2.4	4.3	2.5
CIH	1.275	-0.7	0.4	1.8	2.1	1.1	AlO	1.618	4.9	1.8	0.5	2.1	1.3
CH	1.120	-1.0	0.1	2.6	2.4	1.2	ClO	1.570	3.3	2.5	1.4	4.7	3.2
SH	1.341	-0.8	0.3	1.7	2.0	1.1	BO	1.205	-1.5	1.1	0.6	1.5	0.4
PH	1.422	-0.8	0.2	1.9	2.0	1.0	CN	1.172	-0.8	-3.1	0.5	1.3	0.2
BH	1.232	-0.6	0.1	2.9	2.0	1.0	PN	1.491	-2.4	3.1	0.6	1.6	0.2
SiH	1.520	-0.3	0.4	2.2	2.2	1.3	SiN	1.572	1.1	-2.2	0.2	1.4	0.4
BeH	1.343	0.4	0.4	1.7	1.0	0.5	CIN	1.614	2.9	1.8	0.8	3.8	2.5
AlH	1.648	0.3	0.7	2.5	2.4	1.5	SN	1.494	4.2	-3.9	1.4	2.9	1.4
LiH	1.596	2.5	2.8	2.5	2.0	1.6	N ₂	1.098	-1.8	3.0	1.1	1.9	0.7
NaH	1.887	1.4	1.6	-0.7	0.3	-0.2	C ₂	1.243	0.2	1.8	1.1	1.9	1.1
H ₂	0.741	-1.5	-0.5	2.9	0.9	0.2	O ₂	1.208	-3.3	3.3	0.5	2.7	0.6
BF	1.263	-0.2	1.5	0.5	1.8	0.9	B ₂	1.590	-8.2	-7.0	1.3	2.2	1.7
CF	1.272	-0.4	1.5	0.4	2.6	1.2	F ₂	1.412	-4.7	0.6	-1.7	1.6	-0.6
BeF	1.361 ³⁶	0.2	1.5	0.1	1.3	0.6	P ₂	1.893	-1.8	2.2	0.7	1.9	0.6
NF	1.317	-1.1	1.0	-0.7	2.2	0.5	S ₂	1.889	-0.6	1.7	1.6	3.6	2.0
OF	1.354 ³⁷	-2.0	-0.7	-1.4	2.0	0.0	Cl ₂	1.988	0.1	1.4	1.3	4.5	2.7
SiF	1.601	0.2	1.7	1.1	2.6	1.6	Si ₂	2.246	-4.6	-3.3	-3.8	-2.1	-3.3
PF	1.590	0.3	2.0	1.2	3.1	1.8	Be ₂	2.452 ²⁸	88.4	60.4	-2.0	0.2	2.6
AlF	1.654	-0.3	0.9	0.4	1.8	0.9	Li ₂	2.673	5.0	4.1	2.3	2.1	1.9
CIF	1.628	-1.0	2.0	0.9	4.1	2.2	Na ₂	3.079	3.6	2.9	-3.5	-1.0	-1.3
SF	1.596 ³⁸	0.0	2.1	1.2	3.7	2.0	LiF	1.564	-0.6	0.4	-1.4	-0.2	-0.8
CO	1.128	-1.3	2.0	1.1	2.0	0.9	LiCl	2.021	2.5	2.4	0.9	2.1	1.7
NO	1.151	-2.1	-0.7	0.8	2.2	0.7	NaF	1.926	-2.1	-0.3	-3.0	-0.8	-1.8
BeO	1.331	-2.7	2.2	0.1	1.3	-0.2							

nearly as good (errors $\leq 5\%$). DFT methods have previously been found to perform well for these properties, even for difficult molecules such as Be₂.^{26,27} It is known that even Hartree–Fock calculations can provide good predictions of the higher energy derivatives.^{9,11} Reasonably good predictions (errors $\leq 5\text{ cm}^{-1}$ for hydrides and $\leq 1\text{ cm}^{-1}$ for nonhydrides) of the first anharmonicities ($\omega_e x_e$) are obtained with all the Morse-based estimations that employed self-consistent methods. All methods do poorly in predicting $\omega_e x_e$ for Be₂ (Tables III and IV), for which the experimental value²⁸ is supported by high-level calculations.^{29–31} We did not pursue larger basis sets or higher levels of theory because our goal here is not to describe diatomic molecules but to develop techniques that will be useful for large molecules (for which experimental data are unavailable).

By far the least reliable method is the correlated UMP2 technique; its statistics are dominated by a few extremely bad values. Unreasonable UMP2 vibrational frequencies have been ascribed to spin contamination that depends strongly upon the bond length³² or to geometry-dependent instabilities in the reference UHF wave function.³³ Using a spin-restricted reference improves the results for problematic open-shell molecules.³⁴ UMP2 and ROMP2 results are compared in Table V for the molecules with UMP2 errors $|(\omega_{\text{calc}} - \omega_{\text{expt}})/\omega_{\text{expt}}| > 20\%$ (Table II), for SN (large error in $\omega_e x_e$, Table III), and also for three molecules for which there is reasonably good agreement with experiment (B₂, PH, and SiH). Be₂ is not included in Table V because it is a closed-shell molecule; it is problematic because of the well-known near-degeneracy between the 2s and 2p orbitals, which

TABLE II. Errors in Harmonic Vibrational Frequency ω_e . Experimental Values from Ref. 35 Unless Otherwise Noted.

	Expt. (cm ⁻¹)	Deviation from expt. (%)						Expt. (cm ⁻¹)	Deviation from expt. (%)				
		UHF	UMP2	SVWN	BLYP	B3LYP			UHF	UMP2	SVWN	BLYP	B3LYP
FH	4138.3	5.3	-2.4	-5.1	-7.9	-3.9	SiO	1241.6	13.3	-5.3	-1.7	-5.5	0.3
OH	3737.8	6.9	0.0	-4.4	-6.8	-2.5	PO	1233.3	13.8	232.2	-1.9	-6.8	-0.1
NH	3282.3	7.5	2.5	-4.3	-5.6	-1.3	SO	1149.2	14.7	-4.3	-2.9	-9.9	-2.6
ClH	2990.9	6.5	1.9	-3.3	-5.1	-1.5	AlO	979.2	-17.4	-21.6	2.2	-4.0	-3.0
CH	2858.5	7.0	2.8	-5.5	-6.1	-1.9	ClO	853.8	-2.6	0.1	5.1	-7.5	-2.4
SH	2711.6	7.0	2.4	-3.7	-5.5	-1.5	BO	1885.7	11.0	2.4	0.5	-2.6	1.8
PH	2365.2	8.1	3.5	-3.1	-4.6	-0.8	CN	2068.6	-4.2	38.4	4.0	0.4	4.4
BH	2366.9	6.2	3.5	-6.2	-4.9	-1.3	PN	1337.2	18.8	-13.9	1.1	-2.7	3.5
SiH	2041.8	6.8	3.8	-4.3	-5.4	-1.5	SiN	1151.4	-20.5	28.3	2.4	-2.6	1.6
BeH	2060.8	4.4	3.5	-2.8	-1.8	0.4	CiN	827	-1.0	2.9	5.6	-5.5	-0.9
AlH	1682.6	5.2	3.3	-4.8	-5.6	-2.0	SN	1218.7	-26.6	9.3	0.4	-5.8	0.6
LiH	1405.7	0.8	-0.8	-2.8	-2.4	-0.4	N ₂	2358.6	16.9	-7.8	2.1	-1.0	4.2
NaH	1172.2	2.2	0.8	0.8	-1.6	1.2	C ₂	1854.7	4.6	2.7	3.3	-0.7	2.0
H ₂	4401.2	5.6	3.0	-3.9	-0.6	1.2	O ₂	1580.2	26.5	-10.8	4.2	-4.0	5.0
BF	1402.1	4.9	0.0	0.6	-3.7	-0.0	B ₂	1051.3	35.5	28.7	0.0	-5.1	-3.5
CF	1308.1	7.7	2.1	3.0	-5.1	0.6	F ₂	916.6	35.8	9.9	19.1	8.1	16.3
BeF	1265.93 ³⁹	4.1	1.1	2.5	-0.5	1.8	P ₂	780.8	16.3	-8.5	0.8	-3.9	2.1
NF	1141.4	11.5	4.4	8.4	-2.2	4.1	S ₂	725.6	12.1	-3.8	-2.6	-10.4	-3.2
OF	1053.03 ³⁷	11.5	46.7	13.1	1.5	7.9	Cl ₂	559.7	7.1	-2.2	-2.9	-13.4	-7.0
SiF	857.2	7.2	3.4	2.8	-2.8	1.5	Si ₂	511	16.1	8.6	7.7	0.1	5.9
PF	846.8	8.1	2.6	3.3	-4.1	1.2	Be ₂	275.82 ²⁸	-86.8	-82.2	36.6	15.9	0.7
AlF	802.3	7.5	4.7	3.5	-0.6	2.8	Li ₂	351.4	-3.2	-3.1	-4.8	-5.6	-2.8
CIF	786.1	16.3	2.0	3.0	-7.6	-0.2	Na ₂	159.1	-1.1	-0.3	1.5	-2.7	0.8
SF	837.631 ³⁸	10.0	2.3	3.1	-6.1	0.3	LiF	910.3	13.3	10.0	11.8	7.7	10.8
CO	2169.8	12.4	-2.3	0.2	-2.9	1.8	LiCl	643.3	-2.2	-1.0	-0.7	-3.1	-1.7
NO	1904.2	16.6	105.6	3.4	-2.3	4.6	NaF	563	5.2	3.3	2.6	-4.1	0.4
BeO	1487.3	17.1	-6.5	2.4	-1.3	4.1							

results in strong multireference character. Although ROMP2 performs fairly well, readily available *ab initio* software packages do not currently include analytic derivatives beyond the gradient, making ROMP2 impractical for routine use at the present time. In Table V we also indicate the stability of the UHF reference in the UMP2 calculations and the derivative $d\langle S^2 \rangle/dR$ of the UHF reference evaluated at the UMP2 geometry by central differences ($\Delta R = 0.001 \text{ \AA}$). Although the “problem” molecules do tend to have larger values of $d\langle S^2 \rangle/dR$, there is little correspondence between the errors in the spectroscopic constants and the magnitude of the distance-dependence of the spin contamination. Computed infrared absorption intensities may exhibit pathologies and are included in Table V. The UMP2 and ROMP2 vibrational intensities agree only for B₂ (zero by symmetry) and for the well-behaved molecules PH and SiH.

Current theoretical understanding is still insufficient to provide reliable predictions of pathologies in UMP2 force constants. For example, unphysical values of ω_e may be obtained even with an apparently stable UHF reference (Table V). The association with distance-dependent spin contamination, $d\langle S^2 \rangle/dR \gtrsim 0.05 \text{ \AA}^{-1}$, is useful but lacks a clear theoretical basis.³² Similarly, it is well-known that MP2 frequencies are usually lower than uncorrelated ones;⁸ this is illustrated in Table VI for the singlet molecules in this study. The reverse situation is unusual and suggests a problematic system.³² To illustrate this, the frequency ratios $\omega_{\text{UMP2}}/\omega_{\text{UHF}}$ are listed in Table V.

We can add more empirical associations. From Table V it appears that the ratio of infrared absorption intensities calculated at the UMP2 and UHF levels, $I_{\text{UMP2}}/I_{\text{UHF}}$, is greater than 1 in problematic cases and is usually less than 1 in well-behaved cases. For comparison, the intensity ratios $I_{\text{ROMP2}}/$

TABLE III.
Errors in Vibrational Anharmonicity $\omega_e x_e$ [Eq. (4)]. Experimental Values from Ref. 35 Unless Otherwise Noted.

	Expt. (cm ⁻¹)	Deviation from expt. (cm ⁻¹)					Expt. (cm ⁻¹)		Deviation from expt. (cm ⁻¹)				
		UHF	UMP2	SVWN	BLYP	B3LYP			UHF	UMP2	SVWN	BLYP	B3LYP
FH	89.88	7.9	11.3	12.9	13.8	11.9	SiO	5.97	-0.6	0.4	0.0	0.0	-0.2
OH	84.88	9.5	11.3	8.7	11.4	10.6	PO	6.56	3.8	12783.9	-0.2	-0.0	-0.3
NH	78.35	8.1	4.7	6.6	9.7	8.3	SO	5.63	0.4	-0.6	0.7	0.5	0.6
ClH	52.82	8.7	11.6	3.6	5.3	4.1	AlO	6.97	-1.9	-6.4	-1.6	-1.0	-0.3
CH	63.02	6.7	7.8	5.5	7.8	7.0	ClO	5.5	0.8	-4.0	-0.3	0.2	-0.1
SH	59.9	-5.7	-4.0	0.9	3.5	0.4	BO	11.81	-0.3	-2.0	0.1	0.4	0.2
PH	44.5	2.5	4.1	-3.7	-1.8	-0.4	CN	13.09	16.5	5.5	-0.3	0.3	0.1
BH	49.39	3.6	6.5	3.3	6.2	5.4	PN	6.98	-1.5	2.6	-0.9	-0.7	-1.0
SiH	35.51	2.6	3.4	5.2	6.7	6.9	SiN	6.47	13.0	2.6	-0.4	-0.2	-0.2
BeH	36.31	-0.2	5.3	2.9	4.7	3.5	CiN	5.1	1.4	-0.8	0.2	0.7	0.4
AlH	29.09	0.7	9.9	5.1	5.9	2.7	SN	7.28	0.6	45.3	-0.6	-0.5	-0.5
LiH	23.2	-0.9	-0.9	0.6	1.1	0.6	N ₂	14.32	-2.1	4.5	-0.3	0.0	-0.6
NaH	19.72	-1.7	-3.0	-0.1	1.8	0.4	C ₂	13.34	-1.1	-1.8	-1.7	-1.0	-1.2
H ₂	121.34	35.3	29.9	29.4	35.6	35.2	O ₂	11.98	-0.9	5.2	0.1	-0.2	-0.2
BF	11.84	0.5	0.4	1.0	0.8	0.7	B ₂	9.35	-2.2	-1.5	-0.8	0.0	-0.0
CF	11.1	1.0	-1.8	1.2	0.8	1.0	F ₂	11.24	-4.3	-2.0	-4.2	-4.6	-4.5
BeF	9.3532 ³⁹	0.4	0.1	0.8	0.8	0.7	P ₂	2.84	-0.5	0.7	-0.4	-0.4	-0.4
NF	8.99	1.5	0.0	1.0	0.3	0.9	S ₂	2.84	-0.3	0.6	0.1	0.2	0.1
OF	9.903 ³⁷	7.8	40.0	-1.7	-2.3	-1.7	Cl ₂	2.68	0.1	0.1	-0.3	-0.5	-0.3
SiF	4.74	0.3	0.0	0.3	0.5	0.3	Si ₂	2.02	0.0	0.4	0.3	0.2	0.1
PF	4.49	0.3	0.6	0.5	0.5	0.5	Be ₂	26.024 ²⁸	-23.5	-25.1	-19.0	-17.2	-15.7
AlF	4.77	0.1	-0.2	-0.1	-0.1	-0.2	Li ₂	2.61	-0.6	-0.5	-0.5	0.1	-0.1
CiF	6.16	-2.1	-1.5	-1.5	-1.8	-1.9	Na ₂	0.73	-0.3	-0.2	-0.5	-0.3	-0.4
SF	4.4731 ³⁸	0.0	0.3	0.4	0.4	0.3	LiF	7.93	3.0	3.0	3.8	3.2	3.3
CO	13.29	-0.9	1.2	0.4	0.7	0.1	LiCl	4.5	0.2	-0.5	0.0	-0.1	-0.1
NO	14.08	11.2	716.9	-0.3	-0.1	-0.6	NaF	3.4	1.7	1.6	1.7	1.1	1.5
BeO	11.83	-1.0	1.9	-0.9	-0.9	-0.6							

I_{RHF} for the singlet, heteronuclear molecules in this study are included in Table VI. This ratio is less than 1 in nearly all these well-behaved cases. The observation may be rationalized by noting that the HF dissociation limit is too ionic, resulting in an exaggerated dependence of dipole moment upon bond length. Including correlation (e.g., at the MP2 level) removes much of the spurious charge separation.

Values of the first anharmonicity constant $\omega_e x_e$, estimated using the Morse model function, are generally within a few wave numbers of the experimental values, even though the calculated second derivatives at the HF level of theory are usually higher than the corresponding experimental values. Two reasons for this are apparent: (1) because $\omega_e x_e$ is small in magnitude, an appreciable fractional change may still be less than 1 cm⁻¹; and (2) the anharmonicity prediction depends upon the ratio of the third and second derivatives of the potential energy rather than their absolute values [eq. (4)], so that errors in the second and third

derivatives cancel partially when the derivative ratio is evaluated. Furthermore, the ratio U'''/U'' is less sensitive to bond length than are the individual derivatives, alleviating some of the difficulties associated with the choice of reference geometry.¹¹ For example, the experimental RKR potential for N₂ is characterized at r_e by $(dU''/dr)/U'' = -7.39 \text{ \AA}^{-1}$ and $(dU'''/dr)/U''' = -5.88 \text{ \AA}^{-1}$. The fractional derivative $(d\omega_e x_e/dr)/\omega_e x_e = 3.02 \text{ \AA}^{-1}$ [from eq. (4)] is only half as large.¹¹ We tested this numerically by comparing B3LYP/6-31G(d) derivatives and corresponding values of $\omega_e x_e$ evaluated at computed and experimental geometries r_e . Although the values of the derivatives often changed by 10%, values of $\omega_e x_e$ typically changed by less than 1 cm⁻¹.

The empirical estimates provided by eqs. (5)–(7) have negligible cost and perform nearly as well (Table IV) as the expensive semiempirical methods discussed earlier. Eq. 5 is the simplest, since it requires nothing beyond the harmonic frequency. However, eq. 7 is somewhat more effective and

TABLE IV.
Summary of Deviations from Experiment for 53 Molecules. Values in Parentheses Exclude One Molecule.

Physical quantity	Error measure	HF	MP2	SVWN	BLYP	B3LYP
Bond length r_e (Be ₂)	Mean (%)	1.4 (−0.2)	2.1 (1.0)	0.8 (0.8)	2.0 (2.1)	0.9 (0.9)
	MUE ^a (%)	3.2 (1.6)	2.7 (1.6)	1.5 (1.5)	2.2 (2.2)	1.3 (1.2)
	SD ^b (%)	12.4 (2.1)	8.3 (1.6)	1.5 (1.5)	1.3 (1.3)	1.1 (1.1)
Harmonic frequency ω_e (Be ₂)	Mean (%)	5.0 (6.8)	7.3 (9.0)	1.7 (1.0)	−3.3 (−3.7)	0.9 (0.9)
	MUE ^a (%)	11.6 (9.9)	13.9 (12.4)	4.4 (3.8)	4.6 (4.4)	2.6 (2.7)
	SD ^b (%)	16.5 (10.4)	38.0 (36.2)	6.9 (5.0)	4.5 (3.7)	3.8 (3.8)
Anharmonicity $\omega_e x_e$, 14 hydrides, eq. (4) (H ₂)	Mean (cm ^{−1})	5.5 (3.2)	7.0 (5.2)	5.8 (4.0)	8.0 (5.9)	6.9 (4.7)
	MUE ^a (cm ^{−1})	6.7 (4.5)	8.1 (6.4)	6.3 (4.6)	8.2 (6.1)	6.9 (4.8)
	SD ^b (cm ^{−1})	9.7 (4.7)	8.3 (5.3)	7.9 (4.2)	8.9 (4.3)	9.0 (4.0)
Anharmonicity $\omega_e x_e$, 39 nonhydrides, eq. (4) (Be ₂)	Mean (cm ^{−1})	0.6 (1.2)	347.9 (357.7)	−0.6 (−0.1)	−0.5 (−0.1)	−0.5 (−0.1)
	MUE ^a (cm ^{−1})	2.7 (2.2)	350.4 (359.0)	1.3 (0.8)	1.1 (0.7)	1.1 (0.7)
	SD ^b (cm ^{−1})	5.7 (4.2)	2047.0 (2073.5)	3.3 (1.2)	3.0 (1.2)	2.7 (1.1)
Empirical methods (no <i>ab initio</i> calculations involved)		Eq. (5)	Eq. (6)	Eq. (7)	Parameter values ^c	
$\omega_e x_e$ hydrides, using expt. ω_e (H ₂) ^d	Mean (cm ^{−1})	0.0 (0.0)	1.0 (1.4)	0.0 (0.0)	$a = 0.0287$ (0.0256), $b = -20.0$ (−13.5)	
	MUE ^a (cm ^{−1})	4.8 (3.5)	5.4 (5.6)	4.6 (3.3)	$A = 0.0201$ (0.0203)	
	SE ^e (cm ^{−1})	6.9 (4.8)	6.2 (6.3)	5.8 (4.5)	$A' = 0.0220$ (0.0252), $B = -6.3$ (−14.0)	
$\omega_e x_e$, nonhydrides, using expt. ω_e (Be ₂) ^d	Mean (cm ^{−1})	0.0 (0.0)	−0.7 (−0.2)	0.0 (0.0)	$1000a = 4.87$ (6.82), $b = 2.6$ (−0.2)	
	MUE ^a (cm ^{−1})	2.3 (1.4)	1.7 (1.1)	2.0 (1.1)	$A = 0.0189$ (0.0185)	
	SE ^e (cm ^{−1})	4.2 (1.7)	4.1 (1.6)	3.9 (1.5)	$A' = 0.0133$ (0.0167), $b = 2.8$ (0.9)	

^aMean unsigned error relative to experimental values.
^bSample standard deviation.
^cParameter a is unitless, b and B are in cm^{−1}, and A and A' are in amu^{1/2}.
^dParameters reoptimized with molecule excluded.
^eStandard error of least-squares fit.

only requires the reduced mass in addition to the frequency.

Conclusions

For stretching vibrations, combining analytic second and third derivatives with a Morse model potential leads to useful predictions for the vibrational anharmonicity constant. Of the five semiempirical theories tested, that based upon UMP2 is

the least reliable. For each failure of UMP2, spin-restricted ROMP2 was found to work well. Self-consistent UHF, SVWN, BLYP, and B3LYP are much more robust than UMP2. Purely empirical estimations are competitive with the Morse model approach and are much less expensive. Further studies are needed to determine how these empirical and semiempirical approaches are best generalized to polyatomic molecules.

Several criteria are useful in identifying anomalous semiempirical results for vibrational con-

TABLE V.
Comparison of RMP2 and UMP2 for Selected Molecules (Errors Relative to Experiment). UMP2 Values in Parentheses.

Molecule	r_e (% error)	ω_e (% error)	$\omega_e x_e$ (error in cm^{-1})	MP2 IR int. (km/mol)	UHF stable?	$d\langle S^2 \rangle / dR$ (\AA^{-1}) ^a	ω_e ratio UMP2 / UHF	IR int. ratio UMP2 / UHF
PO ($^2\Pi$)	2.7 (−0.3)	−5.5 (232.2)	−0.2 (12,783.9)	4.2 (91,231)	no	1.45	2.92	1336.
NO ($^2\Pi$)	2.3 (−0.7)	−0.5 (105.6)	−2.0 (716.9)	6.3 (2725)	yes	1.25	1.76	39.2
OF ($^2\Pi$)	0.7 (−0.7)	3.4 (46.6)	−1.1 (39.6)	36.0 (119.8)	yes	0.3	1.31	3.21
CN ($^2\Sigma^+$)	2.8 (−3.1)	−12.4 (38.4)	8.7 (5.5)	120.7 (20.4)	yes	3.2	1.44	1.51
SiN ($^2\Sigma^+$)	2.0 (−2.2)	−7.1 (28.3)	−5.4 (2.6)	3.6 (359.4)	yes	2.9	1.61	8.58
AlO ($^2\Sigma^+$)	3.6 (1.8)	−16.6 (−21.6)	−2.7 (−6.4)	67.5 (1117)	no	0.0	0.95	24.2
SN ($^2\Pi$)	0.8 (−3.9)	8.1 (9.3)	1.3 (45.3)	11.4 (56.6)	yes	2.9	1.49	2.40
B ₂ ($^3\Sigma_g^-$)	0.2 (0.4)	6.8 (6.9)	−1.1 (−1.3)	0 (0)	no	0.0	1.16	
PH ($^3\Sigma^-$)	0.1 (0.2)	4.2 (3.5)	2.8 (43.6)	134.9 (132.7)	yes	0.0	0.96	0.81
SiH ($^2\Pi$)	0.4 (0.4)	3.9 (3.8)	3.3 (35.0)	361.9 (359.6)	yes	0.0	0.97	0.80

^aFor the UHF wave function, evaluated at the UMP2 r_e .**TABLE VI.**
Comparison of RMP2 and RHF Harmonic Vibrational Frequencies and Infrared Absorption Intensities for Singlet Molecules.

Molecule	$\omega_{\text{MP2}} / \omega_{\text{HF}}$	I_{MP2}^a	$I_{\text{MP2}} / I_{\text{HF}}$	Molecule	$\omega_{\text{MP2}} / \omega_{\text{HF}}$	I_{MP2}^a	$I_{\text{MP2}} / I_{\text{HF}}$
FH	0.93	91.1	0.64	PN	0.72	7.9	35.05
ClH	0.96	15.1	0.62	N ₂	0.79	0	
BH	0.98	352.2	0.90	C ₂	0.98	0	
AlH	0.98	659.1	0.82	F ₂	0.81	0	
LiH	0.98	146.4	0.76	P ₂	0.79	0	
NaH	0.99	210.0	0.77	Cl ₂	0.91	0	
H ₂	0.98	0		Be ₂	1.35	0	
BF	0.95	139.2	0.80	Li ₂	1.00	0	
AlF	0.97	83.8	0.73	Na ₂	1.01	0	
ClF	0.88	11.6	0.45	LiF	0.97	111.1	0.79
CO	0.87	25.8	0.19	LiCl	1.01	114.5	0.88
BeO	0.80	25.1	0.23	NaF	0.98	67.7	0.97
SiO	0.84	2.4	0.03				

^aIn km/mol.

stants, although there are exceptions for each criterion. Since UMP2 results are not robust, we recommend that at least some of the criteria be examined before endorsing UMP2 vibrational constants: (1) the calculated values of ω_e and $\omega_e x_e$ should not deviate substantially from the empirical relations of eqs. 5 and 6; (2) harmonic frequencies calculated at the MP2 level should be smaller than those calculated at the corresponding HF level, $\omega_{\text{MP2}} / \omega_{\text{HF}} \leq 1.00$; (3) vibrational absorption intensities calculated at the MP2 level should be smaller than those calculated at the corresponding HF level, $I_{\text{MP2}} / I_{\text{HF}} < 1$; (4) a large distance-dependence of the spin contamination, $d\langle S^2 \rangle / dR \geq 0.05 \text{ \AA}^{-1}$, suggests that calculated constants are too high; (5) testing the stability of the HF reference is only marginally useful.

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